STRUCTURES OF SCHIFF BASE CHELATES OF TRANSITION AND NON-TRANSITION METAL IONS

by

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The structures of Schiff base chelates of twenty-one transition and non-transition metal ions have been discussed on the basis of spectroscopic, magnetic and dielectric properties.

It is well known [19, 44, 52, 56, 58, 65, 66, 73, 76] that with N-substituted salicylaldimines a great number of metal ions form chelate complexes of various compositions and stereochemistry. In previous papers we have dealt with the bonding and the stereochemical behaviour of the Co(II), Ni(II) [27] and Cu(II) [28] Schiff base chelates. In this paper the stereochemical problems of mononuclear chelate complexes of transition and non-transition metal ions of bi- and tetradentate salicylaldehyde derivatives are reviewed on the basis of their spectroscopic, magnetic and dielectric properties. It is quite impossible to summarize the whole literature of Schiff base metal complexes, and therefore we discuss only several characteristic examples.

Discussion

The examples are to be found in the order of increasing oxidation numbers of the metal ions.

Be(II) complexes. ANGEL ET AL. [1] have studied the dielectric behaviour of the Be[HSAL-NR]$_2$* (R=CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9, *s*-C_4H_9 or *t*-C_4H_9) type complexes. For the complexes with R=*n*-alkyl the $_AP$ values are within experimental error of the mean value of 28 cm^3. As R is changed from *n*-C_4H_9 to *i*-C_4H_9 and *s*-C_4H_9 to *t*-C_4H_9, $_AP$ decreases to about one third of this value. For R=*i*-C_3H_7 $_AP$ is less than that observed when R=*n*-C_3H_7. The *i*-C_4H_9, *s*-C_4H_9 and

**Abbreviations.* DMFA dimethylformamide; pn=1,3-diaminopropane; HSAL=salicylaldehydato anion; XSAL=ring-substituted salicylaldehydato anion; HSALH=neutral salicylaldehyde; HSAL-NR=N-R-substituted salicylaldiminato anion; HSAL-NR=N-R-substituted salicylaldimine; HSALen=bis(salicylaldehyde)ethylenediiminato dianion; HSALen-NRR'=N, N-RR'-ethylenesalicylaldiminato anion.

t-C_4H_9 complexes have dipole moments significantly lower than those for the other compounds. This has already been taken as evidence for distortion towards the non-polar planar conformation in the case where R = t-C_4H_9, and it is very likely that a similar, but smaller distortion is present for the other branched-chain butyl groups. The molecular models indicate [1] that steric interactions which would inhibit bending about the metal ligand bond do occur when the alkyl chain contains secondary and tertiary carbon atoms, and consequently this would result in a larger value for the bending force constant and a smaller value of $_AP$ observed.

Zn(II), Cd(II) and Pb(II) complexes. GARNOVSKII ET AL. [37] have studied the i.r. spectra and the dielectric properties of the M[XSAL-N-2-OH-YC_6H_3]$_2$ type complexes (M = Zn(II), Cd(II) and Pb(II)). The dipole moment values of these chelates are to be found between 3.92 and 5.3 D and it has been concluded that these Schiff base chelates have terahedral arrangements. BRAITHWAITE ET AL. [16, 17] examined the u.v. spectra of Zn(II) and other metal chelates and the following assignments of bands were given: $\pi \rightarrow \pi^*$: 44 kK; n $\rightarrow \pi^*$: 41 kK; $\pi \rightarrow \pi^*$ (often as a doublet): 37 kK; $\pi \rightarrow \pi^*$: 27 kK.

Pd(II) and Pt(II) complexes. All the Pd(II) complexes of the type Pd[XSAL-NR]$_2$ (X = H, 3-OCH_3 or 5,6-benzo and R = i-C_3H_7, n-C_3H_7, i-C_4H_9, t-C_4H_9 or substituted phenyls) are diamagnetic [87]. SACCONI ET AL. [68] prepared many compounds of the type Pd[HSAL-NR]$_2$ (R = CH_3, C_2H_5, n-C_3H_7 or n-C_4H_9) and concluded that they are trans-planar [36].

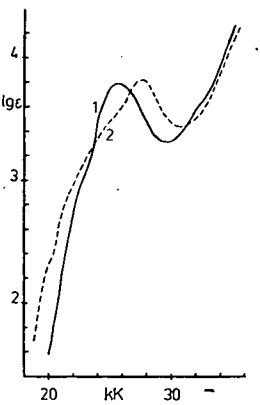


Fig. 1. Visible spectra of 1: Pd[HSAL-N-n-C_4H_9]$_2$ and 2: Pd[HSAL-N-t-C_4H_9]$_2$ measured in $CHCl_3$

Electronic spectra of these complexes show an absorption band at about 25.5 kK, which may be due to an intra-ligand transition [Fig. 1]. The ligand-field bands mainly due to the Pd(II) ion are hidden by the strong bands of other origins. With R = 2,6-$(CH_3)_2C_6H_3$ the steric conditions are not quite favorable for the square-planar configuration, but since the corresponding Ni(II) and Cu(II) complexes have been found to be square-planar [*e.g.* 84], the same configuration also appears most likely [57, 82] for these Pd(II) complexes. For the t-C_4H_9 complex the steric condition is considered to be highly unfavourable for the planar configuration; their spectra are obviously different from those of the n-alkyl complexes.

The configurations of the t-C_4H_9 and i-C_3H_7 complexes are found to be different in many respects from those for the corresponding Ni(II) complexes. This difference may be considered to arise from the following two points:

(a) the ionic radius of the Pd(II) ion is larger than that of the Ni(II) ion, and

(b) the stability of the planar configuration *vis-a-vis* the tetrahedral one is higher for the Pd(II) than for the Ni(II) ion.

The spectra of all these Pd(II) complexes in donor solvents are nearly the same as those measured in non-donor solvents; their configuration may also be retained in pyridine. The Pd(II) ion has a lower tendency to form six-coordination than the Ni(II) ion.

In these respects, the Pt(II) ion is similar to the Pd(II) ion; the difference between the Pt(II) and Ni(II) ions is known to be even more marked than that between the Pd(II) and the Ni(II) ions. Therefore, with the Pt(II) complexes a similar result to that for the corresponding Pd(II) complexes may be expected. This is borne out by the electronic spectra of these Pt(II) complexes. The spectra of the Pt(II) *n*-alkyl complexes are similar to those of the Pt(II) *i*-C_3H_7 complexes but different from those of the *t*-C_4H_9 derivatives.

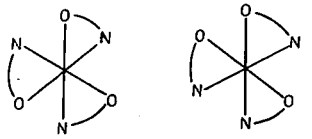
Al(III) complexes. Complexes of the type Al[XSAL-N-n-alkyl]$_3$ (X=H, 5-Br or 3-OCH_3 and alkyl=CH_3, C_2H_5 or *n*-C_3H_7) have been isolated by KUMA and YAMADA [51], but attempts to obtain complexes with R=*i*-C_3H_7, *t*-C_4H_9 or aryl were not successful. This may be due mainly to the steric factors, since the ionic radius of Al(III) (0.57 Å) is much smaller than those of the other transition metal ions.

These tris-complexes display similar electronic spectra, regardless of the nature of *R*. The bands due to intraligand transitions are shifted very slightly towards higher frequencies, indicating the weak Al(III)-ligand bond. The i.r. ν(C=N) bands at about 1620 cm^{-1} indicate that the ligands are coordinated as bidentate ones in their deprotonated form. The N-CH_3 resonance appears as a sharp singlet at about 6.78 and 6.84 ppm for X=H and 5-Br, respectively. The *mer* isomer would be unambigously identified by three equally intense signals for the N-CH_3 groups, as was found to be the case with the corresponding Co(III) and V(III) complexes [45, 64]. The PMR spectra of Al[HSAL-N-CH_3]$_3$ and Al[5-Br-SAL-N-CH_3]$_3$ are found to be consistent with the *fac* form having three-fold symmetry; an X-ray structural study has also revealed [51] that Al[HSAL-N-CH_3]$_3$ is a six-coordinate Al(III) complex having a *fac* configuration.

Y(III) complexes. Y(III) forms chelate complexes of the type YCl_3[HSALH-NR]$_3$ (R=CH_3, C_2H_5, *n*-C_3H_7 or *i*-C_3H_7) with N-alkylsalicylaldimines [50]. The complexes are stable in the solid state, but in solution they undergo decomposition in various ways. The electronic spectra in DMSO show well-defined absorption bands at about 25.5—26.0 and 31.7—31.9 kK, which are considered to be due to electronic transitions within the Schiff base molecules. These bands are found to be shifted towards very slightly higher frequencies, as compared with those of the free ligand and the $UO_2(NO_3)_2$[HSALH-NR]$_2$ complexes [86], respectively. The i.r. spectra show the ν(C=N) band of the ligands at about 1635—1640 cm^{-1}, so the above complexes contain neutral salicylideneimines, HSALH-NR. Based upon the experimental arguments, these chelates may be formulated as [YCl_2(HSALH-NR)$_3$]Cl, in which the Y(III) ion probably achieves a coordination number of eight with three bidentate Schiff base molecules. The hydrogen bonding may occur either between the two adjacent ligands, or within one base molecule; the latter possibility seems much less likely.

V(III) complexes. RÖHRSCHED ET AL. [64] have prepared V(III) chelates of the type V[XSAL-NR]$_3$ (R=CH_3 and X=H; R=*n*-C_3H_7 and X=H, 3-, 4- or 5-CH_3). These complexes exhibit large isotropic proton contact shifts, which unequivocally demonstrate the *trans* stereochemistry for all. No amount of *cis* isomer was detected in any case. These complexes contain three identical, unsymmetrical chelate rings

and can therefore exist as *cis* and/or *trans* isomers in which like donor atoms are arranged *fac*ially or *mer*idianly (*a*), respectively. Hence, the *cis* isomer will produce



a)

one signal for each ring substituent (H, CH_3), while three signals should occur in principle for each substituent of the *trans* isomer. The PMR spectra demonstrate unequivocally the *trans* stereochemistry for all the above complexes.

Cr(III) complexes. Tris(salicylaldehydato)Cr(III) reacts with primary amines to give complexes of the formula Cr[HSAL-NR]$_3$ (R=*n*-C_3H_7, *i*-C_4H_9, 4-$CH_3C_6H_4$ or 4-BrC_6H_4). The complexes are monomeric in benzene [26]; their magnetic moments are to be found between 3.7 and 3.9 B.M. Assuming that the compounds have octahedral symmetry, two spin-allowed transitions are expected, *viz.* $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$. The Δ values (Table I) place the ligands between oxalate (17 500 kK)

Table I

Magnetic moments of Cr[XSAL-NR]$_3$ type complexes [26]

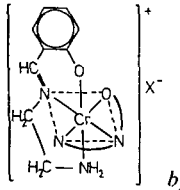
R	B. M.	10 Dq
n-C_3H_7	3.77	18 000
i-C_3H_7	3.80	17 950
4-CH_3-C_6H_4	3.80	17 700
4-Br-C_6H_4	3.81	17 700
Cr[HSALen]$_2ClO_4$	3.71	——

and ethylenediamine (21 880 kK) in the spectrochemical series. The true $^4T_{1g} \leftarrow {}^4A_{2g}$ transition is obscured in this region and the bands could not be resolved further.

The Cr[XSAL-NR]$_3$ type complexes (X=H or 5,6-benzo, and R=CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7 or C_6H_5) have magnetic moments of about 3.79—3.86 B.M. at room temperature [78]. Although the two types of configuration, a *mer*- and a *fac*-form, are possible for these complexes, only one form of the two was isolated as crystals. It is likely that all these Cr(III) complexes assume the same type of configuration, since they show nearly identical absorption spectra. It is interesting to note that the complexes with R=*i*-C_3H_7 can also be prepared, since it was believed to be very difficult due to the steric hindrance to synthesize the corresponding Co(III) complexes [85].

The [Cr(HSALen)L_2]X.nH_2O type complexes [77] (L=H_2O, NH_3, $H_2NC_2H_5$, *n*-$NH_2C_3H_7$, *n*-$NH_2C_4H_9$ or CN^-; X=Cl^- or K^+; n=1, 1.5 or 2) at room temperature show magnetic moments of 3.80—3.85 B.M., which corresponds to three unpaired electrons, as expected for octahedral chromium(III) compounds. The i.r.

spectra of these complexes are similar to those of the corresponding Co(III) complexes of the type [Co(HSALen) L_2]X [83]. According to O'CONNOR and WEST [26] these complexes have a cationic structure with the tridentate ligand (*b*) $^-O.C_6H_4.CH=$ $=N(CH_2)H_2NH_2$.



b)

Mn(III) complexes. Complexes of Mn(III) and N-substituted salicylaldimines of general formulae Mn[HSAL-NR]$_3$ and Mn[HSAL-NR]$_2$X (X=Cl^-, Br^- or Ac^-) show high-spin magnetic behaviour with small deviation of the susceptibilities from the CURIE law [9], and the moments are independent of temperature. Complexes of the type Mn[HSALen]X (X=Br^- or I^-) have also been studied.

The ^5D ground state of the high-spin Mn(III) splits in octahedral and axial crystal fields; the ^5E_g term lies lowest in octahedral symmetry and should give rise to magnetically simple behaviour [35]. The moment differs from the spin-only value for four unpaired electrons (4.9 B.M.) by the factor ($1-2\lambda/10Dq$), due to mixing in of the $^5T_{2g}$ term into the ^5E_g through spin-orbit coupling (Table II). The diffuse reflec-

Table II

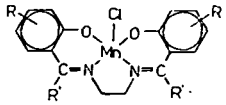
Solid state magnetic moments of several Mn(III) Schiff base chelates [9]

Complex	B. M.	Complex	B. M.
Mn[HSAL]$_3$	4.86	Mn[HSAL-N-*n*-C_3H_7]$_2$Ac	4.99
Mn[HSAL-N-*n*-C_3H_7]$_3$	5.00	Mn[HSAL-N-*i*-C_3H_7]$_2$Ac	4.92
Mn[HSAL-N-*c*-hexyl]$_3$	4.86	Mn[HSAL-N-*n*-C_3H_7]$_2$Cl	5.04
Mn[HSAL-N-$CH_3C_6H_5$]$_3$	4.95	Mn[HSAL-N-*n*-C_3H_7]$_2$Br	4.87
Mn[HSAL-N-C_6H_5]$_3$	4.81	Mn[HSALen]Br	4.75
Mn[HSAL-N-4-Br-C_6H_4]$_3$	4.83	Mn[HSALen]I	4.80

tance spectra show bands at 5—13 and 15—25 kK. The near-infrared bands have been assigned to the transition $^5B_1 \leftarrow {}^5A_1$ arising from axial distortion of the ground level ^5E_g [29] and to the spin-forbidden $^3T_{1g} \leftarrow {}^5E_g$ transition [53]. The positions of these bands are in agreement with those observed by DINGLE [30] for other Mn(III) derivatives. The splitting of the bands is most likely due to the JAHN-TELLER effect and this has been observed in numerous studies [30, 53, 63].

Reaction of nitric oxide with Mn^{II}[HSALen] causes oxidation, and compounds of the type Mn[HSALen](OAc) can be obtained. The effective magnetic moments at room temperature are a little below the value of 4.90 B.M. expected for high-spin Mn(III) compounds [31]; the reduction in the moment and its temperature variation can be ascribed to antiferromagnetic interaction [31].

A series of five-coordinate complexes of the type Mn[SB]Cl (SB is the tetradentate 4-X-HSALen; X=H, CH_3, *s*-C_4H_9, OAc^- or Br^-) have been prepared [15]; the complexes are presumably square-pyramidal (*c*) with axial Cl ligands [38].



c)

Fe(III) complexes. VAN DEN BERGEN ET AL. have discussed N-substituted salicylaldimine Fe(III) complexes of the type Fe[HSAL-NR]$_3$ (I), $FeCl_3$[HSALH-NR]$_2$ (II) and Fe[HSAL-NR]$_2$X (III) [7] and examined their magnetic properties [10]. All the complexes show spin-free magnetic behaviour; the moments are of the order of 5.85—6.15 B.M. (Table III). The (I) type complexes are trigonally distorted octahedral.

Table III

Magnetic moments of different spin-free iron(III) chelates [7]

Compound	B. M.
Fe[HSAL-N-*n*-C_3H_7]$_3$	5.9
Fe[HSAL-N-*n*-C_4H_9]$_3$	5.9
Fe[HSAL-N-benzyl]$_3$	5.85
Fe[HSAL-N-*n*-C_3H_7]$_2$Cl	5.9
Fe[HSAL-N-*n*-C_4H_9]$_2$Cl	6.05
Fe[HSAL-N-C_6H_5]$_2$Cl	6.0
Fe[HSALH-N-C_2H_5]$_2$	5.9
Fe[HSALH-N-C_6H_5]$_2$	5.95

The chelates (II) may be formulated as [Fe(HSALH-NR)$_2$Cl]Cl$_2$ and the moments show a great dependence on temperature, which may be due to a zero-field splitting between the three low-lying KRAMER doublets. The (III) type complexes (X=Cl or Br) have reduced moments of about 5.2 B.M. due to weak antiferromagnetic interactions [54].

With $FeCl_3$ HSALen forms a dark red-brown chelate complex which has a dimeric structure [Fe(HSALen)Cl]$_2$ [41]. The octahedral coordination of each metal atom is completed by a single covalent iron-chlorine bond. Recrystallization of the dimer from nitromethane yields crystals of monomeric Fe[HSALen]Cl with a five-coordinate, square-pyramidal structure [40].

The magnetic moments of Fe(III) chelates of HSALen derivatives [39] and those of the carboxylate complexes of the type Fe[HSALen]L (L=acetate, phenylacetate, benzoate, p-nitrophenylacetate, chloroacetate, dichloroacetate, trichloroacetate or trifluoroacetate) [55] are reported by several authors.

Some other behaviour of Fe(III) chelates is described in the literature [*e.g.* 4, 12, 32].

Co(III) complexes. Co(III) chelate complexes may easily be prepared by the oxidation of a Co(II) complex [74]. Japanese authors have synthetized and investi-

gated several Co(III) chelates of the type Co[XSAL-NR]$_3$, where R=*n*-alkyl [59, 60] or branched alkyl [85]. All the complexes are diamagnetic. The electronic spectra of the complexes Co[HSAL-N-*n*-alkyl]$_3$ are quite similar to each other, irrespective of the length of the *n*-alkyl chain. The band appearing in the visible can be assigned to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition in the notation of the octahedral symmetry.

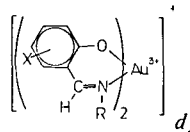
Six-coordinated metal complexes containing three unsymmetrical bidentate ligands can exist in two geometrically isomeric forms: *cis* (C_{3v}) and *trans* (C_{2v}). The above chelates can be isolated only in the sterically less hindered *trans* form, as proved by the nuclear magnetic resonances [21] and dipole moments [25]. The bands due to the spin-allowed $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow$ transitions in fields of appropriate lower symmetry are split. In the *cis* form no splitting of the bands is expected; for crystal-field purposes the *cis* isomer is essentially cubic [92]. In the *trans* form all term components have different energies [2] and, in principle, multiple bands are predicted.

Co[HSAL-N-CH_3]$_3$ shows bands at about 15.63 and 17.54 kK due to the $^1B_2 \leftarrow {}^1A_1$ and $^1B_1 \leftarrow$ transitions. The spectrum of Co[HSAL-N-C_2H_5]$_3$ is similar to that of the CH_3 analogue, but with a smaller splitting, while in the spectrum of Co[HSAL-N-C_4H_9]$_3$ only one broad band [Fig. 2] is observed [23].

Two configurations, a *mer*- and a *fac*-form, are possible for the tris-chelates discussed, but only the *mer*-form is usually found [*e.g.* 25].

Some other types of Co(III) complexes, *e.g.* Co[XSAL-N-Y-OH]$_3$ [81], Na[Co(CN)$_2$(SB)] (SB=tetradentate Schiff base anions) [33], tris(N-alkyl-2-hydroxypropiophenimine)Co(III) [20] have been synthetized and studied from spectroscopic, magnetic and nuclear resonance [21, 22] aspects. The resonance spectra also provide unequivocal evidence for the existence of the *trans (mer)* isomer.

Au(III) complexes. Au(III) complexes (*d*) of the type [Au(XSAL-N-alkyl)$_2$].



d)

[$AuCl_2$] have been prepared [88] (X=5-Cl, alkyl=CH_3; and X=H or 5,6-benzo, alkyl=C_2H_5, *n*-C_3H_7, *i*-C_3H_7 or *n*-C_4H_9). These complexes are all diamagnetic. In the region 15—30 kK the ion $[AuCl_2]^-$ exhibits no absorption, so the spectra may be considered to represent those due to the complexes $[Au(XSAL\text{-}N\text{-}alkyl)_2]^+$ [Fig. 3]. That the solution spectra are similar to each other indicates that all these complexes have a square-planar configuration. The broad band appearing in the range 17—24 kK may be assigned to the spin-allowed d-d transitions in the planar complexes. The intense band at about 27 kK may be due to the intra-ligand transitions.

For the complexes of the $[Au(XSAL\text{-}N\text{-}i\text{-}C_3H_7)_2]^+$ type, steric hindrance against the planar configuration may be expected to be high. The corresponding Ni(II) and Cu(II) complexes are tetrahedral or planar, depending upon X, but the above Au(III) complexes have a planar configuration, since their spectra are similar to those of the complexes of *n*-alkyl type. This difference between the Au(III) ($5d^8$) and the Ni(II) ($3d^8$) complexes may be interpreted principally by the bonding nature and the size

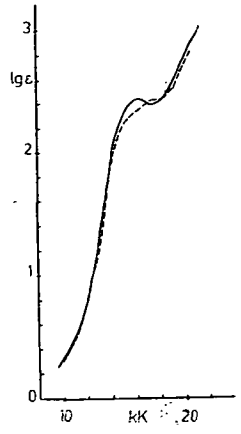


Fig. 2. Absorption spectra of
1: $Co[HSAL\text{-}N\text{-}n\text{-}C_4H_9]_3$ in benzene;
2: $Co[HSAL\text{-}NCH_3]_3$ in toluene

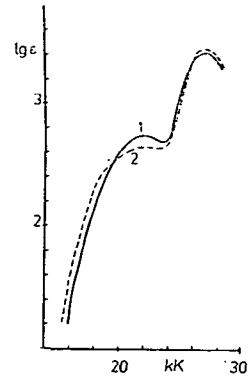
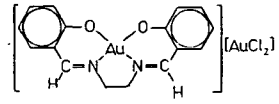


Fig. 3. Absorption spectra of Au(III) complexes.
1: $[Au(HSAL\text{-}N\text{-}n\text{-}C_3H_7)_2][AuCl_2]$ in cloroform;
2: $[Au(5\text{-}Cl\text{-}SAL\text{-}N\text{-}CH_3)_2][AuCl_2]$ in acetone

of the metal ions, as was discussed in the case of the corresponding Pd(II) and Pt(II) complexes [82, 87, 89].

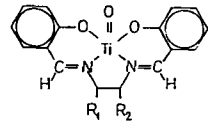
The synthesis of several Au(III) complexes, *e.g.* $[Au(HSALen)][AuCl_2]$ (*e*) and



e)

others, are reported by INAZU [46]; these complexes also have square-planar arrangements.

Ti(IV) complexes. GULLOTTI and PASINI [42] have synthetized several oxotitanum(IV) chelates with tetradentate Schiff bases (*f*) produced by the condensation of



f)

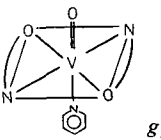
salicylaldehyde with optically active polymethylenediamines. They have investigated the electronic spectra, i.r. spectra, conductivities and circular dichroisms of these chelates and have concluded that in the solid state they contain polymeric Ti-O-Ti-O chains, as is suggested by their extremely low solubility and the low νTiO stretching band. Two classes of compounds were obtained: compounds *A* with one equivalent of acid per mole of complex, and compounds *B* which did not contain any acid.

In some instances the conformation of the chelate ring is comparable with that of compounds of the VO(IV) ion [61], as in the case of the (-)pn derivatives, but usually they are more complicated.

The electronic spectra of TiO[HSAL-(-)pn] and its perchloric acid derivative show a band at about 380 nm, which has been assigned to the $\pi \rightarrow \pi^*$ transition of the azomethine groups [14], shifted to lower energy than in the free ligand [43], as is usually the case in this type of complex [14, 61]. Another weak shoulder at about 450 nm appears in the DMFA and pyridine solution spectra of the perchloric acid adduct. Interestingly, the methanol solution of the type *A* derivative yields the same spectrum as that of the corresponding type *B*. From pyridine or DMFA the form with anionic perchlorate is obtained; the weak shoulder at 450 nm is probably related with the direct protonation of the complex.

V(IV) complexes. Many $VO[XSAL\text{-}NR]_2$ type complexes have been obtained [79] (X=H or 3-OCH_3; R=CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_3H_7, $CH(CH_3)C_2H_5$, $CH_2CH(CH_3)_2$ or c-hexyl). All the *n*-alkyl complexes show similar electronic spectra in the solid state and in non-donor solvents [Fig. 4], and it is considered that they assume a square-pyramidale configuration, even for R=α-branched alkyls. The two groups of XSAL-NR most probably assume a nearly *trans*-planar configuration.

The complexes in pyridine show spectra which are different from the spectra of the same complexes in the solid state and in non-donor solvents. The change on going from non-donor solvets to pyridine is not very large, but quite characteristic. This fact seems to indicate that the VO(IV) complexes, when dissolved in pyridine, combine with one molecule of pyridine to form six-coordinated solvates (*g*).



g)

The complexes of R=α-branched type in chloroform and in the solid state show spectra quite similar to those of the corresponding complexes with R=*n*-alkyl. It is

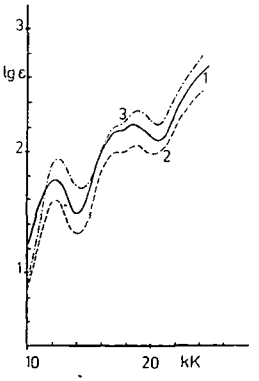


Fig. 4. Reflectance spectra of 1: $VO[HSAL\text{-}N\text{-}C_2H_5]_2$; 2: $VO[HSAL\text{-}N\text{-}n\text{-}C_4H_9]_2$; 3: $VO[HSAL\text{-}N\text{-}CH_2CH(CH_3)_2]_2$

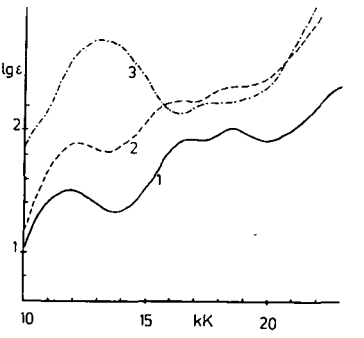


Fig. 5. Spectra of VO(IV) complexes. 1: $VO[HSAL\text{-}N\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2$ in pyridine; 2: $VO[HSAL\text{-}N\text{-}C_6H_5]_2$ in reflection; 3: $VO[5\text{-}Br\text{-}SAL\text{-}N\text{-}C_6H_5]_2$ in reflection

therefore most likely that for all these complexes the coordination of two ligands may be nearly planar. The spectra measured in pyridine are quite different from the spectra of the same complexes in chloroform and in the solid state. It is most likely that this anomalous change of the spectra of these α-branched derivatives is due to the steric hindrance leading to a distorted configuration for the pyridine solvates.

When R is phenyl or 3- or 4-substituted phenyl causing very little steric hindrance, the $VO[XSAL\text{-}NR]_2$ type complexes are expected to have a square-pyramidal configuration [49]; the two XSAL-NR groups most probably have a nearly planar configuration [67, 79]. The spectra are similar to each other and also to those of the N-alkyl derivatives [79]. For $R=2\text{-}CH_3.C_6H_4$, $2,6\text{-}(CH_3)_2C_6H_3$ or $2,6\text{-}(C_2H_5)_2C_6H_3$, a significant distortion from the square-pyramidal configuration does not occur, since their absorption maxima [Fig. 5] in the solid state and in non-donor solvents are nearly the same as those of $VO[XSAL\text{-}NC_6H_5]_2$. These substituted phenyl derivatives in pyridine form sixcoordinate pyridine adducts having a more distorted configuration than that of the corresponding adduct of the phenyl derivative.

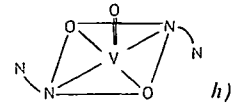
The V(IV) ion seems to take up an additional ligand such as pyridine to form a six-coordinate adduct more readily than do the corresponding Co(II), Ni(II) and Cu(II) ions.

The reflectance spectra of $VO[5\text{-}Cl\text{-}SAL\text{-}NC_6H_5]_2$ and $VO[5\text{-}Br\text{-}SAL\text{-}NC_6H_5]_2$ [Fig. 5, curve 3] differ remarkably from those of the other complexes such as $VO[HSAL\text{-}NC_6H_5]_2$. Moreover, their magnetic moments are lower than the spin-only moment of 1.73 B.M. for the d^1 system, showing that some sort of interaction may be present between the V(IV) ions. The probable configuration for these two complexes in the solid state is a binuclear one.

With ring-substituted salicylaldehydes and N-substituted ethylenediamines, VO(IV) forms chelate complexes of two different types [67]: $VO[XSALen\text{-}NRR']_2$ and $(XSAL)[XSALen\text{-}NRR']VO$. Compounds of the first type are formed when one or both substituents R and R′ are aryl groups and when R and R′ are both ethyl groups. The compounds are paramagnetic, with magnetic moments in the range 1.7—1.9 B.M. [3]. Two typical compounds with $X=H$ and $R=R'=C_2H_5$ have been found to be monomers in chloroform solution. The i.r. spectra of compounds of this series contain a strong band characteristic of the V=O group at 950—1000 cm^{-1} [6, 71, 75].

The reflectance spectra show three bands in the crystal-field region, at 11.50—12.00, 16.65—16.95 and 18.20—19.05 kK, respectively. The spectra of the chloroform solutions show bands at practically the same frequencies as in the reflectance spectra. The spectra of the solutions in pyridine are notably different. The first band is shifted to 13.70—13.80 kK, the position of the second band is virtually unchanged, while the third is slightly displaced towards the violet.

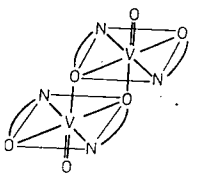
VO(IV) usually shows coordination number 5 or 6 in its complexes, with coordination geometries corresponding to a tetragonal pyramid or a distorted octahedron [69], respectively. In the proposed structure the vanadium is surrounded by a *trans* N_2O_2 set and the terminal nitrogen atoms of the *en* chains are not linked to the metal (*h*). This is supported by the fact that the spectra of two typical salicylaldimino com-



h)

plexes, $VO[HSAL\text{-}NCH_3]_2$ and $VO[HSAL\text{-}NC_6H_5]_2$, in which the set of coordinating atoms is in all probability trans, when dissolved in inert solvents, are quite similar to those of complexes of this series.

The $VO[XSAL\text{-}N\text{-}Y\text{-}O]_2$ type complexes have subnormal magnetic moments (0.87—1.36 B.M.) [48], similarly to the corresponding Cu(II) complexes [47, 80]. These low moments are considered to be due to an exchange interaction between V(IV) ions, and it is very likely that these VO(IV) complexes have a binuclear structure (*i*).

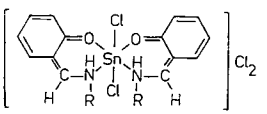


i)

Other examples may be seen in the excellent review of SELBIN [70].

Sn(IV) complexes. Organotin(IV) chelates with tetradentate Schiff bases of the type $R_2Sn[HSALen]$ ($R=CH_3$ or C_6H_5) have been synthetized by VAN DEN BERGEN ET AL. [8]. The ^1H NMR spectra of the chelates suggest that the *R* groups are *cis* to each other, while the HSALen ligand assumes the unusual twisted configuration. A number of other Sn(IV) Schiff base complexes with bi- and tetradentate ligands have also been described [8].

The i.r. spectrum of $SnCl_4[HSALH\text{-}N\text{-}p\text{-}CH_3C_6H_4]_2$ shows a band at about 1640 cm^{-1}, similar to those for the complexes $CoCl_2[HSALH\text{-}NR]_2$ [5, 72] and $FeX_3[HSALH\text{-}NR]_2$ [7], where it was proposed that the ligand was bidentate and in the keto-amine form. The strong band at 314 cm^{-1} is attributed to the ν(Sn-Cl) vibration of six-coordinated tin(IV). The most probable structure for these complexes is $[SnCl_2(HSALH\text{-}N\text{-}p\text{-}CH_3C_6H_4)]Cl_2$, which involves a six-coordinate cation and bidentate chelation of the keto-amine Schiff base (*j*).



j)

Pb(IV) complexes. With the Pb(IV) ion bidentate Schiff bases form chelate complexes of the type $PbCl_2[XSAL\text{-}NR]_2$ [13]. These complexes are non-electrolytes. On the basis of their u.v. and i.r. spectra a six-coordinate structure is most likely. The electronic spectra are very similar to each other; the band at about 240—250 nm may be assigned to the $\pi \rightarrow \pi^*$ transitions of the benzene nucleus [24]. The intensities of these $\pi \rightarrow \pi^*$ bands increase with increasing electron-releasing effects of the 4-X substituents [62]. The ν(C=N) bands appear at about 1610—1630 cm^{-1}.

Nb(V) and Ta(V) complexes. Nb(V) and Ta(V) pentachlorides react with N-aryl-salicylaldimines to produce alkoxo complexes with the neutral Schiff base coordinated, $MCl_3(OR')_2[HSALH\text{-}NR]$ [91] ($R=C_6H_5$ or $4\text{-}CH_3C_6H_4$; $R'=CH_3$ or C_2H_5). The intense band at about 1640 cm^{-1} is higher than those due to ν(C=N) in complexes with deprotonated bidentate Schiff base or the free ligand. A similar band has

been observed for Co(II), [5], Fe(III) [7], Sn(IV) [11, 34] and WO_2(VI) [90] complexes. The CH=N signal appears as a singlet in the range 9.10—9.25 ppm, at slightly lower fields compared with that for the free ligand. A broad singlet, which is presumably due to the O··H··N resonance, occurs in the range 10.0—13.5 ppm.

It may be more reasonable to assume that these complexes have six-coordination structures containing the neutral Schiff base, which is coordinated to the metal ion as a unidentate ligand through the oxygen atom.

W(VI) complexes. The reaction of WO_2Cl_2 with N-aryl-salicylaldimines has yielded dioxotungsten(VI) complexes of the type WO_2Cl_2[HSALH-NR]$_2$ [90] (R= =C_6H_5, 4-$CH_3C_6H_4$ or 4-ClC_6H_4). The complexes are all diamagnetic. They exhibit i.r. absorption bands at about 895—915 cm^{-1} and 940—960 cm^{-1}, which may be assigned to W=O stretching. It is considered [90] that these dioxotungsten(VI) complexes have a *cis* tungstenyl O=W=O structure with no bridging W=O=W structure. The complexes show a band at about 1640 cm^{-1}, which is assigned to ν(C=N) vibration of the neutral Schiff bases.

Various structures may be proposed [90], *e.g.* the W(VI) ion can achieve six-coordination either with two oxygen atoms, unidentate Schiff bases and coordinated

Table IV

Summary of the structural characteristics of the discussed metal chelates

M	Coord. number	Magnetism	Ligand coord.	Structure*		
				n-alkyl (phenyl)	branched alkyl	en deriv.
Be(II)	4	Dia	HSAL-N-	t-pl.	d.-pl.	
Zn(II)	4	Dia	HSAL-N-	tetr.	d.-tetr.	
Cd(II)	4	Dia	HSAL-N-	tetr.	d.-tetr.	
Pb(II)	4	Dia	HSAL-N-	tetr.	d.-tetr.	
Pd(II)	4	Dia	HSAL-N-	t-pl.	t-pl.	
Pt(II)	4	Dia	HSAL-N-	t-pl.	d.-pl.	
Al(III)	6	Dia	HSAL-N-	oct./fac		
Y(III)	8	Dia	HSALH-N-	dodec.		
V(III)	6	Para	HSAL-N-	oct./mer		
Cr(III)	6	Para	HSAL-N-	oct./mer	oct./mer	
Mn(III)	5	Para	HSAL-N-		s-pyr.	s-pyr.
	6	Para	HSAL-N-	oct./mer		
Fe(III)	5	Para	HSAL-N-	s-pyr.	s-pyr.	s-pyr.
			HSALH-N-			
	6	Para	HSAL-N-	d.-oct.		
Co(III)	6	Dia	HSAL-N-	oct./mer	oct./mer	d.-oct.
Au(III)	4	Dia	HSAL-N-	t-pl.	t-pl.	s.-pl.
Ti(IV)	5	Dia	HSAL-N-			s-pyr.
V(IV)	5	Para	HSAL-N-	s-pyr.	s-pyr.	s-pyr.
Sn(IV)	6	Dia	HSALH-N-	d.-oct.		d.-oct.
Pb(IV)	6	Dia	HSAL-N-	d.-oct.		
Nb(V)	6	Dia	HSALH-N-	d.-oct.		
Ta(V)	6	Dia	HSALH-N-	d.-oct.		
W(VI)	6	Dia	HSALH-N-	d.-oct.		

* t-pl. = trans-planar; d.-pl. = distorted planar; tetr. = tetrahedral; d.-tetr. = distorted tetrahedral; oct. = octahedral; dodec. = dodecahedral; s-pyr. = square-pyramidal; d.-oct. = distorted octahedral; s.-pl. = square-planar; en = ethylenhediamine.

chloride ions, or with two oxygen atoms, bidentate Schiff bases and non-bonded chloride ions. It seems likely [90] that they may have a similar structure to that of the type $WO_2Cl_2(L)_2$ [18].

Table IV summarizes some structural characteristics of the chelates discussed. It is important to note that these findings may not be generalized for other metals and/or other Schiff base ligands.

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СТРУКТУРА ХЕЛАТОВ ШИФФОВЫХ ОСНОВАНИЙ МЕТАЛЛОВ ПЕРЕМЕННОЙ И ПОСТОЯННОЙ ВАЛЕНТНОСТИ

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Обсуждена структура хелатов шиффовых оснований 21 металла переменной и постоянной валентности на основании изученных спектроскопических, магнитных и диэлектрических свойств.